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VII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

SIXTH PAPER.

THE ACTION OF BROMINE ON TOLUOL AND SOME OF ITS DERIVATIVES.

By C. Loring Jackson and A. W. Field.

Presented June 12, 1878.

The history of the action of halogens on toluol begins with the discovery of toluol by Pelletier and Walter, who say in their paper,[*] published in 1838, on "retinnaphte" (toluol) from coal tar, that by distilling it repeatedly in a stream of chlorine there was formed a brownish-yellow oil with a sharp taste, a very strong smell somewhat like that of horse-radish, and a powerful action on the eyes, whose formula, founded on a doubtful analysis, was $C_7H_6Cl_2$, and which with potassic hydrate gave potassic chloride and an oil with a different smell. They also tried the action of bromine on boiling retinnaphte, and made in this way a compound similar to the preceding in every respect, but they observed that the cold hydrocarbon was apparently unaffected by chlorine.

Deville[†] was the next to take up the subject in 1841, in his paper on balsam of tolu, from which he obtained a hydrocarbon (benzoene) identical with the retinnaphte of Pelletier and Walter. From this he made the following compounds: C_7H_7Cl, boiling-point 170°, by the action of chlorine on the hydrocarbon when cooled and protected from light; $C_7H_6Cl_4$ in diffused daylight; $C_7H_5Cl_7$ when the chlorine was in excess; $C_7H_6Cl_8$ in direct sunlight; and $C_7H_2Cl_6$ by repeated distillation in an atmosphere of chlorine.

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[*] Ann. Chim. Phys., lxvii. 269.

[†] Ibid., ser. 3, iii. 178.

The next important step was taken by Cannizzaro,[*] in 1855, who proved that the product of the action of chlorine on toluol is identical with benzylchloride made from benzylalcohol. Beilstein,[†] in 1860, introduced a great deal of confusion into the subject by contradicting Gerhardt's[‡] inference from Deville's work, that the action of chlorine on cold toluol was different from its action on hot, and describing experiments of his own to prove that differences in temperature made no difference in the products. He also thought he had proved the identity of the dichlortoluol from toluol and chlorine with the chlorobenzol made from benzaldehyde with phosphoric pentachloride, but Cahours,[§] three years later (1863), announced that they were only isomeric. In the same year (1863), Naquet[‖] studied trichlortoluol in comparison with the product of the action of phosphoric pentachloride on benzoylchloride.

The next important discovery was made in 1865 by Fittig and Glinzer,[¶] who obtained monobromtoluol by treating cold toluol with bromine, and pointed out the marked differences between it and chlortoluol (benzylchloride); while in 1866 Kekule,[**] in his paper on aromatic isomeres described benzylbromide made from benzylalcohol, and, after comparing it with monobromtoluol, explained the cause of their difference.

In this same year (1866), Beilstein, in conjunction with Geitner,[††] put the whole subject on a firm basis by the following statement, since known as *Beilstein's Law:* — *Toluol behaves differently with chlorine according as it is hot or cold;* in the cold, a chlortoluol as stable as chlorbenzol is formed, usually, however, mixed with benzylchloride unless great care is taken in cooling. If hot, the toluol is converted into benzylchloride, but it is not necessary absolutely to boil it, as a very slight increase of temperature is enough completely to prevent the formation of chlortoluol. *With iodine only chlortoluol is formed under all conditions, even when the toluol is boiling;*[‡‡] the chlortoluol obtained by this process is however contaminated with substances containing iodine. In this paper they predict a similar action with bromine, and state that xylol behaves with chlorine like toluol. A paper by Limpricht[*] in the same volume of the *Annalen der Chemie und Pharmacie*, and another by Cannizzaro[†] in the next volume but one, did not advance the subject materially.

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[*] Ann. Chem. Pharm., xcvi. 246.

[‡] Traité de Chimie, iii. 567.

[†] Ibid., cxvi. 336.

[§] Comptes Rendus, lvi. 222.

[‖] Comptes Rendus, lv. 407, lvi. 129.

[¶] Ann. Chem. Pharm., cxxxiii. 47, cxxxvi. 301.

[**] Ibid., cxxxvii. 188.

[††] Ibid., cxxxix. 331.

[‡‡] The use of iodine was suggested by the paper of H. Müller (Journal London Chem. Soc., xv. 41) on making chlorine substitution products from benzol in presence of iodine.

Lauth and Grimaux[‡] in 1867, described a convenient form of the process for making benzylchloride, consisting in passing chlorine into toluol heated to 110°–140° in a flask with a return-cooler. In the same year, Beilstein[§] extended his law to the action of bromine on toluol, which, if iodine was present, gave bromtoluol as the only product with the exception of a little of some iodine compound, even if the toluol was boiling, while without iodine bromine formed with boiling toluol benzylbromide, always, however, mixed with some bromtoluol. Lauth and Grimaux,[‖] on the other hand, could find no bromtoluol in the product obtained by mixing the vapors of bromine and toluol.

Since that time, but little progress has been made in this subject, the papers in which the action of halogens on toluol is mentioned, dealing rather with the products than with the conditions of the action, but the following papers deserve mention: Fittig,[¶] on the formation of bromtoluol free from benzylbromide; Beilstein and Kuhlberg,[**] extending Beilstein's Law to the action of chlorine on the various chlorine compounds of toluol, and one of their later papers[††] (on tetrachlortoluol) in which they direct that 2 or 3 grs. of iodine should be used to make the chlorine enter the ring. This is the only statement of the amount of iodine needed for this purpose that we have been able to find, and even here nothing is said of the amount of toluol to be used with the 3 grs. of iodine.

We have not been more successful in finding definite statements about the temperature at which the bromine begins to enter the side-chain, those authors[‡‡] who mention any temperature, give the boiling-point of the substance to be acted on, or a temperature somewhat above this, with the exception of Wachendorff,[§§] who in studying the action of bromine on para- and metanitrotoluol, found that the benzylbromide was formed as low as 130° in a sealed tube, or at 180° in open vessels, while at its boiling-point the nitrotoluol was almost entirely decomposed by bromine.

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[*] Ann. Chem. Pharm., cxxxix. 303.

[†] Ibid., cxli. 198.

[‡] Ibid., cxliii. 79.

[§] Ibid., cxliii. 369.

[‖] Bull. Chem. Soc., vii. 108.

[¶] Ann. Chem. Pharm., cxlvii. 39.

[**] Ibid., cxlvi. 317; also cxlvii. 339.

[††] Ibid., cl. 286.

[‡‡] Vogt and Henninger, Ann. Chim. Phys., ser. 4, xxvii. 130. Grimaux, Comptes Rendus, lxx. 1363. Radziszewski, Ber. d. ch. G., 1873, p. 492.

[§§] Ann. Chem. Pharm., clxxxv. 259.

In the work described in this paper, we have tried to give a more definite statement to Beilstein's Law, — which may be stated thus: When toluol (or its derivatives) is treated with chlorine or bromine in the cold, the halogen attaches itself to the benzole ring; if hot, to the side-chain; in presence of iodine exclusively to the ring, even when boiling. To do this, we have tried to determine the amount of benzylbromide formed from toluol and some of its derivatives, in the first place at different temperatures, and secondly in presence of different amounts of iodine.

Effect of Differences in Temperature.

In these experiments a weighed amount of toluol or the substituted toluol was heated in a flask with a return-cooler by a paraffine bath, and the calculated quantity of bromine added with a drop-funnel at such a rate that no bromine could be seen in the fumes which escaped through the cooler. The temperature of the bath and of the vapor within the flask was noted throughout the experiment. To determine how much benzylbromide had been formed, we used the following method, which is very similar to that used by Cannizzaro* for the same purpose. The product of the reaction, after being freed from hydrobromic acid by washing first with a dilute solution of sodic carbonate and afterwards with distilled water, was heated to 100° with alcoholic ammonia for two hours; the bromides of ammonium and the three benzylamines thus formed were decomposed by warming with a solution of baric hydrate, and the amount of baric bromide determined by Volhardt's † sulphocyanate method of titration after the organic matter had been filtered out. To test the method of estimating the amount of removable bromine, pure parabrombenzylbromide was treated with alcoholic ammonia and baric hydrate, as described above, and 98 per cent of the calculated amount of bromine obtained. The experiments collected in Table I. were then made.

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* Ann. Chem. Pharm., cxli. 198.

† Ibid., cxc. 1.

TABLE I.

ACTION OF BROMINE ON TOLUOL. BOILING-POINT, 111°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
I.	5 grs.	100°	97°–98°	72.	65
II.	5 grs.	100°	98°–100°	54.	20
III.	10 grs.	100°	97°–98°	55.	60
IV.	10 grs.	100°	95°	65.	55
V.	5 grs.	120°	110°–114°	82.	10
VI.	10 grs.	120°	112°–114°	87.	20
VII.	10 grs.	120°	111°–113°	74.	20

ACTION OF BROMINE ON PARACHLORTOLUOL. MELTING-POINT, 7°; BOILING-POINT, 160°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
VIII.	6.9 grs.	100°	81°–86°	69.	45
IX.	"	120°	110°–113°	80.	
X.	"	140°	130°–135°	92.	20
XI.	"	167°	157°–161°	95.	15

ACTION OF BROMINE ON PARABROMTOLUOL. MELTING-POINT, 28°.5; BOILING-POINT, 185°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XII.	9.4 grs.	100°	87°–92°	51.	
XIII.	"	100°	90°–93°	58.	40
XIV.	"	120°	111°–114°	95.	25
XV.	"	120°	110°–114°	90.	30
XVI.	"	140°	130°–134°	88.	10
XVII.	"	170°	160°–164°	92.	8
XVIII.	"	190°	180°–184°	94.	5

ACTION OF BROMINE ON ORTHOBROMTOLUOL. BOILING-POINT, 182°.

Number of Experiment.	Amount taken.	Temperature.		Per cent of Theory.	Time in Minutes.
		In the Bath.	In the Flask.		
XIX.	9.4 grs.	100°	90°	21.	30
XX.	"	100°	86°–92°	31.	45
XXI.	"	100°	90°	32.	55
XXII.	"	120°	110°–114°	74.	50
XXIII.	"	140°	130°–134°	83.	25
XXIV.	"	170°	160°–164°	84.	10
XXV.	"	190°	180°–184°	84.	15

Before considering the inferences which can be drawn from these results, it is necessary to examine the sources of error which affect the accuracy of the process; and, for this purpose, all the results obtained under the same conditions are collected in Table II.

TABLE II.

Toluol at 100°. 5 grs. used.		
No. of Experiment.	Time in Minutes.	Per cent.
I.	65	72
II.	20	54
Toluol at 100°. 10 grs. used.		
III.	60	55
IV.	55	65
Toluol at 120°. 5 grs. used.		
V.	10	82

Toluol at 120°. 10 grs. used.		
No. of Experiment.	Time in Minutes.	Per cent.
VI.	20	87
VII.	20	74
Parabromtoluol at 120°.		
XIV.	25	95
XV.	30	90
Orthobromtoluol at 100°.		
XIX.	30	21
XX.	45	31
XXI.	55	32

The want of agreement between these results can be ascribed to two causes: first, differences in the rate of adding the bromine; second, unavoidable defects in the method of bromiring or of treating the product. To the first class belong the difference of 18 per cent, corresponding to 45 minutes difference in rate between Nos. I. and II., and that of 10 per cent, corresponding to 15 minutes between Nos. XIX. and XX.; but these are the only differences that come under this class, a difference of less than 10 minutes having apparently no effect upon the amount of benzylbromide formed (see XX. and XXI.). The differences due to the second cause are that of 10 per cent between III. and IV., 13 per cent between VI. and VII., and 5 per cent between XIV. and XV., which show that our method is incapable of giving the exact quantitative results that we had hoped for. The most probable cause of these variations is the difficulty of washing and handling the liquid or pasty product of the bromiring. In the following discussion, Experiment I. will be rejected, because of the very slow rate at which the bromine was added, and differences of less than 10 per cent will be accepted, if at all, only with the greatest caution.

Effect of the Temperature on the Amount of Benzylbromide formed. — To make this comparison easier, the results given in Table I. (reduced to the mean where there are several observations at the same temperature) are collected in the following table, and in the second column, under each substance, the differences between the percentages at each temperature, and at that which immediately follows it, are given.

TABLE III.

Temperature.	Toluol.		Parachlortoluol.		Parabromtoluol.		Orthobromtoluol.	
	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.	Per cent.	Difference.
81°-100°	58		69		54		28	
		23		11		38		46
110°-114°	81		80		92		74	
				12		—4		9
130°-135°			92		88		83	
				3		4		1
160°-164°			95		92		84	
						2		0
180°-184°					94		84	
110°-Bpt.				15		2		10

From this it appears that the bromine begins to enter the side-chain in considerable quantity at about the boiling-point of toluol (111°), and that after this the amount of benzylbromide formed increases with the temperature, although to a much smaller extent, with the exception of parabromtoluol, which is probably due to defects in the process; in fact, the difference between 81°-100° and 110°-114° is greater than that between the latter temperature and the boiling-point of the substance, except in the case of the single series of observations on parachlortoluol.

Some experiments with paraiodtoluol cannot be directly compared with the preceding, because we could find no satisfactory way of removing the iodine set free during the addition of the bromine, and were therefore obliged to content ourselves with weighing the crystals of paraiodbenzylbromide formed. We found, under these conditions, that below 100° no crystals were formed; at about 111°, 18 per cent of the calculated amount was obtained; at 135°, 42 per cent; at 175°, 54 per cent; at 200°, 51 per cent. The low percentages are partly accounted for by the solubility of the paraiodbenzylbromide in the oily secondary products. A similar series with parachlortoluol gave below 100° no crystals; at 111°, 89 per cent of very impure crystals (apparently nearly one half parachlortoluol); at 135°, 98 per cent of purer crystals; at 160°, 89 per cent. These results confirm, in a general way, those obtained by the more accurate method.

The effect of differences in temperature on the rate at which the bromine is taken up will be seen from the following table, in which the mean time needed to bromir equivalent weights of the substances for each temperature is given. In calculating these means, the times of several experiments were used, in which the amount of benzylbromide was not determined; many of them, therefore, depend on a much larger number of observations than the mean amounts given in Table III.

TABLE IV.

Temperature.	Time in Minutes.			
	Toluol.	Parachlortoluol.	Parabromtoluol.	Orthobromtoluol.
81°–100°	26	40	43	43
110°–114°	11	30	27	40
130°–135°		22	10	25
160°–164°		20	8	10
180°–184°			5	15

Although the method of adding the bromine used by us made great differences of rate, under the same conditions, possible, so that all these results must be taken with some caution, it is evident that the rate increases rapidly, and apparently regularly, with the temperature, showing no especially large increase between 81°–100° and 110°–114°, as was the case with the per cent. This rapid increase in the rate suggests the following objection to the results obtained in studying the effect of temperature on the amount of benzylbromide formed; the small percentages of benzylbromide obtained below 100° may have been due to loss of bromine from running the experiment too fast, as the secondary products were not studied; and therefore it is possible that they were the unaltered original substance, and not formed from this by substitution of bromine in the ring; this view is supported by the larger per cent (72) obtained in Experiment I., where the time was 45 minutes longer than in II.; but, on the other hand, it is hardly possible that nearly 5 grs. of bromine could have escaped without giving a perceptible color to about the same quantity of hydrobromic acid, and great pains were taken in every experiment to regulate the addition of the bromine so that the escaping fumes should be perfectly colorless. Even if the amounts of benzylbromide obtained below 100° are rejected on this account, our statement that there is a decided change in the action at 111° still holds good, as in that case the time necessary to take up the bromine below 100° must be greatly increased, and therefore the differences in rate between 87°–100° and 110°–114° would become as great in proportion to the differences between other temperatures as those in the per cents are if our present results are accepted.

We had hoped, in beginning this research, to make a careful comparison of the action of bromine on toluol and its substitution products, but the differences between the results from different substances fall so near the wide limits of error of our process, that we prefer to confine ourselves to the following very general statements. Bromine is taken up by toluol more rapidly than by any of its substitution products studied; orthobromtoluol seems to take up bromine less rapidly than parabromtoluol, and this inference from our quantitative results is confirmed by our experience in the preparation of the substituted benzylbromides in large quantity, when it has been observed invariably that the parabromtoluol absorbed bromine most rapidily, the meta-compound less so, and the orthobromtoluol even more slowly than the meta. In regard to the percentages of benzylbromide formed from each substance we do not feel that our results allow us to make any generalization, as the apparently lower numbers obtained from the orthobromtoluol may be due to differences in working up the product, which in the case of the ortho-compound is a liquid, while the parabromtoluol yields a pasty solid.

We have also tried some experiments with toluol at lower temperatures, and found that at 58°, and even at 0°, a small amount of benzylbromide was formed, as shown by obtaining an amine on treatment of the product with alcoholic ammonia. The rate at which the bromine was taken up was, however, extremely slow, and we feel that these experiments need confirmation.

Effect of the Addition of Iodine.

We were induced to take up this branch of the subject by the observation that paraiodbenzylbromide was formed by the action of bromine on paraiodtoluol, even when the flask was filled with violet vapors of iodine during the addition of the bromine, which contradicted Beilstein's Law as generally understood; but we have not studied it so thoroughly as the effect of differences in temperature, as we could find no sufficiently satisfactory and easy method of determining the amount of benzylbromide formed.

Our best series of results (Table V.) was obtained from parachlortoluol bromired at 160°, the crystals of parachlorbenzylbromide formed being weighed after they had been brought to the melting-point of the pure substance, 48°.5.

TABLE V.

Per cent of Iodine added.	10 grs. Parachlortoluol yielded.	Per cent of possible Amount.
1	6.5 grs.	51
5	3. grs.	23
10	No crystals.	

The product of the last experiment was washed, boiled with alcoholic sodic acetate, and then heated in a sealed tube with aqueous ammonia, when crystals of the parachlorbenzylalcohol were obtained, showing that even in presence of 10 per cent of iodine a portion of the bromine enters the side-chain. This result was confirmed by some experiments on toluol, in one of which toluol was mixed with 10 per cent of iodine and treated with chlorine at 120°; on fractioning the product, about one half passed over from 164°–222° (chlortoluol boils from 156°–160°), attacked the nose violently, and gave an amine when heated in a sealed tube with alcoholic ammonia; it must, therefore, have contained benzylchloride, boiling-point 176°, and probably chlorbenzylchloride, boiling-point 213°. In another experiment it seemed that even 40 per cent of iodine was not enough to completely prevent the formation of benzylbromide at 111°; but the determination of the benzylbromide by the amine process was interfered with by the presence of iodine substitution products to such an extent that we can place but little reliance on this result.

Summary.

I. The portion of Beilstein's Law which states that benzyl-compounds are formed at high, and substituted toluols at low temperatures, is confirmed by our experiments.

II. The benzyl-compound begins to be the principal product near the boiling-point of toluol (111°); in other words, no connection can be traced between the boiling-point of a substituted toluol and the temperature at which the bromine begins to enter its side-chain in quantity. Above 111° there is a gradual increase in the amount formed as the temperature is raised; but the total increase from 111° to the boiling-point of the substance is usually smaller than the increase from 100° to 111°.

III. The rate at which the bromine is taken up becomes more rapid as the temperature is raised.

IV. Toluol takes up bromine more rapidly than its substitution products. This result is confirmed by the observation of Beilstein and Kuhlberg,* that the more chlorine there was attached to the ring, the harder it was to introduce chlorine into the side-chain.

V. The monobromtoluols seem to take up bromine (in the side-chain) in the following order: para most rapidly, meta next, ortho least rapidly.

VI. The portion of Beilstein's Law which states that in presence of iodine no benzyl-compound is formed, even at the boiling-point, is not true when the amount of iodine is 10 per cent or less, and it is probable that toluol yields a little benzylbromide at 111°, even in presence of 40 per cent of iodine.

From our experiments, it follows that the best way of obtaining a benzylbromide is to add the bromine at the boiling-point of the substance used, but it is not well to allow the temperature to rise above this point, as then there is danger of decomposition of the product.

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* Ann. Chem. Pharm., cl. 286.